VARIATIONS IN THE SUPERCONDUCTIVE PROPERTIES OF TANTALUM AS IT BECOMES SATURATED WITH HYDROGEN, V. R. Golik, B. G. Lazarev, and V. I. Khotkevich, Physico-Tech Inst, Acad Sci Ukrainian SSR, "Zhur Eksper i Teoret Fiz", Vol XIX, No 3, March 1949, pp. 202-206

As shown in our laboratory (1), tantalum's superconductive properties depend upon its previous history. Various lattice distortions due to absorbed gases and deformations cause extreme variations in transition temperature (T_k) and change the slope of the curve of critical field (H_k) versus temperature; the true critical parameters of superconductive tantalum, therefore, can be obtained only from degassed stressless specimens. In his report, Webber (2) came to the same conclusion, pointing out, however, that the gas content in tantalum was not the main factor causing different superconductive properties.

Our later studies were conducted to clarify separately the influence of absorbed gases and deformations. The first experiments on hydrogen-saturated tantalum (by electrolysis) demonstrated very sharp changes in superconductive properties of the specimen in proportion to its saturation with hydrogen. This report contains the results of these experiments.

For the study, tantalum was taken in the form of a wire 0.15 mm in diameter with residual resistance of $R_{4.2}/R_{290} = 0.2$. The specimen studied, which was firmly fastened in a special shank, was the cathode in an electrolytic bath with distilled slightly-alkaline water. The cryostat unit permitted the specimen, after electrolysis, to be cooled to the temperature of liquid helium in less than two minutes.

Such a method of measurement was dictated not only by a desire to avoid possible liberation of hydrogen from the specimen before electrolysis ended, but also by the necessity for making the greatest possible number of consecutive measurements as the specimen became saturated with hydrogen. As it proved later, the specimen saturated with hydrogen actually changed its properties only slightly when left in the open at room temperature for a prolonged period (24-48 hours).

Although it retains its metallic ~~glint~~ luster, the tantalum saturated with hydrogen becomes highly brittle and increases considerably in volume (elongated by several percent) (3).

The temperature and magnetic curves of superconductive transitions were measured. The curves of resistance versus temperature for various saturations with hydrogen are shown in Figure 1. The resistance of the specimens is relative to the original resistance of the specimen at 4.2° K. The curves were numbered in order of increasing saturation. This numbering is retained in all figures. In proportion to the degree of saturation by hydrogen, the interval required for the super-conductive transition increased continuously towards lower temperatures, until finally the specimen had lost its superconductive properties. (at any rate, it was not superconducting down to 1.85° K). At the same time, the point where the superconductive transition began still remained unchanged. A slight drop in resistance was observed at the transition temperature of the original tantalum, even for a sample saturated with hydrogen, until superconducivity disappeared. The residual resistance of the most saturated specimen increased more than three ~~times~~ fold in comparison with that of the original tantalum. For comparison, in the same figure there is shown a curve (dotted) of transition for a tantalum specimen which was annealed in a poor vacuum under conditions in which nitrogen and oxygen were absorbed by the tantalum (1). For convenience of observation, the size of this curve has been ~~diminished 10 times in~~ reduced to one-tenth compar~~ison~~ed ~~with~~ to the ~~remaining~~ other curves.

Figure 2 shows in the case of one specimen, the part of the transition curves for the breakdown of superconductivity by a longitudinal magnetic field for various saturations with hydrogen. Here, as in the curves of temperature transition, attention is drawn to the transition and its the unusual elongation which ~~occupies a space~~ takes up a region of hundreds of gausses and which continually ~~expands as~~ increase the metal is saturated with hydrogen.

T_k and H_k become difficult to determine as a consequence of the extreme expansion of both the temperature and the magnetic transitions. The generally-accepted definition of these quantities as the temperature and field at which resistance becomes equal to one-half the residual resistance (which is possibly still applicable to a certain degree for narrow transition intervals) becomes quite unsuitable in this case. This is clearly seen from Figures 1 and 2. As in Figure 1, the curves in this case Figure 2 are stretched out ~~in proportion to~~ as the saturation proceeds, ~~and here~~ towards ~~the~~ lower fields. Consequently, the critical fields, determined according to the point where $R/R_{4.2} = 0.5$, ~~is~~ are displaced toward the lower values. Therefore, the curves of critical field versus temperature for tantalum saturated with hydrogen ~~is~~ are displaced toward still lower temperatures (Figure 3), dH_k/dT increasing meanwhile. If H_k is determined from other points of the transition curves, then a comparison of Figure 2 and 3 shows that other values would be obtained for dH_k/dT. If this determination is made from the part of the transition curve where the resistance is close to the full value, then, as seen from Figure 3, the graph of H_k versus temperature would be practically independent of the degree of saturation; points for all saturations lie on the curve of the original tantalum.

The changes in superconducting properties of tantalum saturated with hydrogen can be linked with the amount of hydrogen. In the measurements conducted, this amount was difficult to determine. A certain quantitative representation of this dependency can be obtained by determining the quantity of hydrogen ~~precipitated~~ on the specimen during electrolysis. The curve of Figure 4 shows the dependence of the width of the temperature interval of the transition upon this amount of hydrogen. The latter depends strongly upon the state of the specimen as was shown by an experiment. A specimen saturated with hydrogen until disappearance of superconductivity and then annealed by a current in a high vacuum at 1700° for 10 hours completely regains its superconducting properties. If this specimen is again subjected to saturation with hydrogen, then its superconductivity will disappear for a much smaller quantity of hydrogen precipitated on the specimen; only approximately 5.10^{-3} milligrams are necessary, instead of approximately 340.10^{-3} milligrams for the same specimen before annealing.

The operations of saturation and annealing lead to reversible results and can be repeated many times. It is interesting to note that a specimen saturated with hydrogen to a certain intermediate state (not up to complete disappearance of superconductivity), when located for a prolonged period of time in air at room temperature, partially regains its in initial properties; i. e., its resistance decreases and T_k is increased. Finally, our studies on the influence of electrolytic saturation with hydrogen on niobium should be mentioned. Niobium was used for superconducting electrodes in our experiments. The experiments demonstrated that the superconductivity of niobium at 4.2° K was retained during prolonged (many hours) saturation with hydrogen.

2. It is known (3), that tantalum absorbs a very ~~great~~ large quantity of gaseous hydrogen. At the same time M. Andrews for example stressed the absence of signs of formation of compounds up to the very high concentrations obtained. On the other hand, Hagg, making an X-ray study of tantalum saturated with hydrogen, established that during this process three homogeneous phases form in succession. These phases have different lattices, all of which however are close to the orginal lattice of tantalum (volume-centered cube, a = 3.298). The tantalum lattice ~~stays as orginally~~ retains its initial characteristics for saturations up to 12 atomic % hydrogen, and only its parameter is increased by 1.7%.

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A study of the superconductive properties of metals under ~~all-sided~~ compression from all sides showed that in tantalum a change in the lattice parameter by approximately 0.02% (corresponding to a pressure of 1370 kg/cm^2) lowered T_k by approximately 0.006°(5). Therefore, if saturation with hydrogen only mechanically extended the tantalum lattice, we should expect a substantial increase in T_k; for example, approximately by 0.4° for 12 atomic % hydrogen.

However, quite the reverse phenomena takes place, which testifies to the fact that hydrogen not only expands the lattice, but also actually changes the electron distribution in the metal; i.e., we may speak of the formation of an alloy or compound. The phase which forms has properties which are quite different from the properties of the usual superconductive alloys and compounds. Actually, as tantalum becomes saturated with hydrogen, the curves become more and more elongated towards weak magnetic fields (Figure 2) or towards low temperatures (Figure 1).

This can be considered as a gradual reduction in temperature of superconductivity during saturation with hydrogen up to that saturation at which superconductivity is lost entirely. Such behavior can be explained more easily by the formation of an unbroken series of alloys with hydrogen than by the formation of definite compounds.

In order to emphasize the peculiarities of the behavior of the system tantalum-hydrogen, obtained in electrolysis, a curve (dotted) is ~~imposed on~~ drawn in Figure 1 for a specimen of tantalum which was annealed in a poor vacuum and which ~~has~~ had consequently absorbed a certain amount of oxygen and nitrogen. The transition depicted by this curve, in contrast to the other curves on Figure 1, is displaced toward a temperature much lower than the transition temperature of the original tantalum.

It is interesting to note that H_k (Figure 3) changes comparatively little as the tantalum is saturated with hydrogen. This fact

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might indicate that the superconductive part in this process ~~is the~~ [illegible] little islands of tantalum which ~~are~~ remain unsaturated by hydrogen. However, for quite strong saturation, this would lead to a large H_k (because of the rapid breaking up of these little islands) which is actually not observed. It is also interesting that saturation of the tantalum with hydrogen does not cause extreme ~~non~~inhomogeneities of the lattice. The latter would also cause a substantial increase of H_k.

In order to understand the general properties of metals so close in chemical relationship as niobium and tantalum, the opposite influence of hydrogen on their superconductive properties seems important. While the ~~superconductive~~ temperature of superconduction rises toward the region of hydrogen temperatures in niobium hydride, in compounds of tantalum with hydrogen superconductivity is lost.

The results of these, for the meantime preliminary, studies showed that the superconductive properties of tantalum are extremely easily affected by ~~sensitive~~ to absorbed gases. Webber's conclusion concerning the slight effect of absorbed gases on the properties of tantalum is erroneous.

A more detailed and quantitative study of the influence of hydrogen absorbed by tantalum will be made later. -- Submitted 29 July 1948

(1) B. Lazarev, V. Khotkevich. ZhETF, 18, 807, 1948.

(2) R. Webber. Phys. Rev., 72, 1241, 1947.

(3) E. Pietsch. ZS. f. Elektrochem., 39, 577, 1933. Mary Andrews. Journ. Am. Chem. Soc., 54, 1845, 1932. E. Harding and D. Smith, ibid., 15, 1508, 1918. A. Sieverts and H. Brunning. ZS. phys. Chem., A, 174, 365, 1935.

(4) G. Hagg. ZS. phys. Chem., B, 11, 433, 1930.

(5) L. Kan. Dissertation, Khar'kov, 1948

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[Figures appended here]

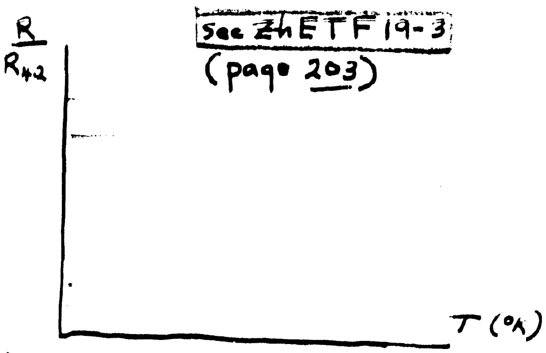

Figure 1. O — original specimen.
1,2,3,4,7 — specimen No 1.
5 — specimen No. 2.
6 — specimen No. 3.

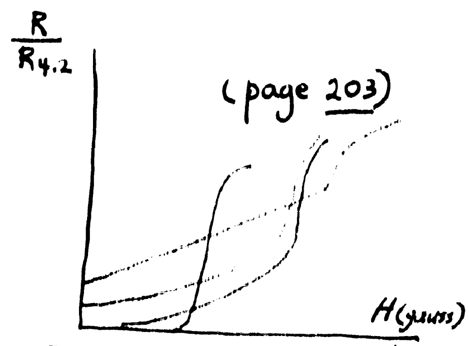

Figure 2. O – T = 3.992°K.
1,2 – T = 3.865°K.
3 – T = 3.805°K.

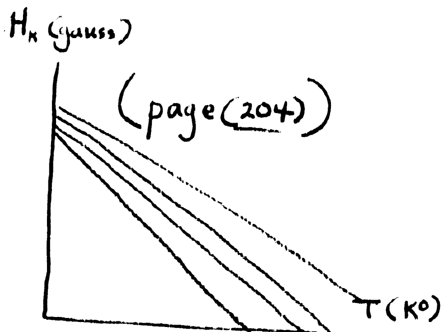

Figure 3. Specimen No. 1.

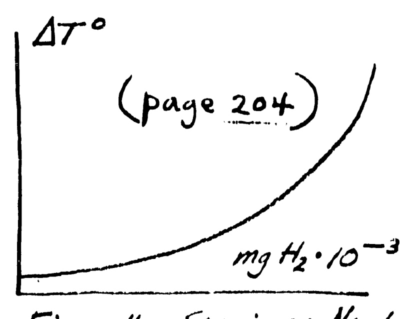

Figure 4. Specimen No. 1.

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